ARL-TR-7900 ● DEC 2016

US Army Research Laboratory

Flexure Strength and Optical Transparency of Magnesium–Aluminate Spinel ($MgAlO_4$): Influence of Polishing and Glass Coating

by Steve M Kilczewski, Robert J Pavlacka, Jeffrey J Swab, Jane W Adams, and Jared C Wright

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

ARL-TR-7900 ● DEC 2016

US Army Research Laboratory

Flexure Strength and Optical Transparency of Magnesium–Aluminate Spinel ($MgAlO_4$): Influence of Polishing and Glass Coating

by Steve M Kilczewski and Jared C Wright
TKC Global, Herndon, VA

Robert J Pavlacka
Oak Ridge Institute for Science and Education, Oak Ridge, TN

Jeffrey J Swab and Jane W Adams
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
December 2016	Technical Report	October 2009–July 2012

4. TITLE AND SUBTITLE

Flexure Strength and Optical Transparency of Magnesium–Aluminate Spinel ($MgAlO_4$): Influence of Polishing and Glass Coating

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Steve M Kilczewski, Robert J Pavlacka, Jeffrey J Swab, Jane W Adams, and Jared C Wright

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

US Army Research Laboratory
ATTN: RDRL-WMM-E
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-TR-7900

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Transparent magnesium–aluminate spinel has been under investigation for numerous transparent applications across a wide-transmission spectrum, including domes and armor windows. Surface polishing is necessary to achieve a transparent product; however, previous work on the flexure strength of spinel shows very little difference between ground or polished specimens. It is desired to increase the flexure strength of spinel. Other mechanisms for strengthening spinel, such as reducing the grain size or eliminating sintering aids, are being investigated. One method that shows some promise is the application of a thin glass coating. This is shown to improve the transparency of unpolished spinel as well as provide an additional avenue for strength improvement by minimizing surface flaws. Results showing increases in strength and transparency are presented.

15. SUBJECT TERMS

flexure strength, spinel, glass coating, optical properties, surface finish

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Steve M Kilczewski
Unclassified	Unclassified	Unclassified	UU	20	19b. TELEPHONE NUMBER (Include area code) 410-306-0753

Contents

List of Figures iv

List of Tables iv

Acknowledgments v

1. Introduction 1

2. Experimental Procedure 2

3. Results and Discussion 4

4. Conclusions 9

5. References 10

List of Symbols, Abbreviations, and Acronyms 11

Distribution List 12

List of Figures

Fig. 1 SEM micrograph showing a representative section of the microstructure of the as-received hot-pressed/HIP'ed spinel plates 2

Fig. 2 Photographs qualitatively showing optical quality of uncoated- and coated-spinel specimens, all of which are in direct contact with the US Army Research Laboratory logo; bars' width is 16.8 mm..... 6

Fig. 3 UV/VIS transmission curves for all of the tested spinel specimens for 200–850 nm wavelengths..... 7

Fig. 4 SEM micrographs of the glass–spinel interface after heat treatment (Table 1); resulting interfaces of each surface-finish type—a) polished, b) ground as per ASTM, and c) HP/HIP'ed—all show existence of interface phases..... 8

Fig. 5 Representative EDS scans across the glass–spinel interface showing relative change in chemical composition across the interface-reaction zone 9

List of Tables

Table 1 The fire and anneal cycle to glass-coat spinel bars in air..... 3

Table 2 Summary of results of flexural-strength testing of coated and uncoated spinel bars; all specimens are the same "oversize" bars described in Section 2..... 5

Acknowledgments

The authors wish to thank the following individuals for their respective efforts toward the completion of this project: Jerry LaSalvia, Eugene Shanholtz, Jian Yu, Rebecca L Walker, and John J Pittari III.

INTENTIONALLY LEFT BLANK.

1. Introduction

Magnesium-aluminate spinel ($MgAlO_4$) is currently being investigated for use in transparent armor packages as a strike-face material. Current commercial approaches for reliably producing large specimens with high transparency necessitate the use of aggressive densification techniques that result in very coarse microstructures (i.e., average grain sizes up to 500 µm with some grains approaching 1 mm in size). As a result of the coarse microstructure, commercial spinels have considerably lower strength than traditional fine-grained spinel. Swab et al. showed that, under the same loading conditions, the flexure strength of coarse-grained spinel was approximately 75 MPa while the strength of a fine-grained (i.e., <25 µm), sintered spinel was close to 200 MPa.[1] The exhibited low strength in the coarse-grained material is limiting the viability for transparent spinel's use in demanding applications where large areal sizes are required.

One method commonly used to increase the strength of a ceramic is surface polishing. It has been well documented that surface finish influences the strength of a ceramic[2–4] and that polishing increases the strength of a material by reducing the size and frequency of strength-limiting surface flaws. This is especially important when the maximum stress is applied at the specimen's surface, such as when the specimen is subjected to a bending load (i.e., flexure). Notably, transparent spinel ceramics must be polished in order to be sufficiently transparent and distortion free to be useful as an optical window. Polishing accounts for 30%–50% of the production cost of large spinel plates. To date, no studies have been conducted that determined the influence of polishing on the strength of these coarse-grained spinel materials. It is expected any approach to strengthen the surface of spinel while reducing or eliminating the polishing requirements would be a significant advance toward robust and affordable, transparent spinel windows.

Glass coating (or glazing) is a common technique used to strengthen ceramics. The use of glazing as a strengthening technique, however, is generally relegated to weak materials such as porcelain and whiteware ceramics.[5] Glass-coating methods have not garnered much attention for use on advanced ceramics for transparent armor packages, although glass coating has been attempted on sapphire[6] and it has been suggested in the field of electro-optics.[7] The use of glazing as a strengthening technique has been investigated for weak, coarse-grained spinel.[8] Flexural-strength enhancement resulting from the addition of a sodium aluminosilicate (SiO_2-BaO-Na_2O-B_2O_3-Al_2O_3) glass coating on coarse-grained transparent spinel having 3 different surface finishes were investigated.

2. Experimental Procedure

Plates of commercially available magnesium–aluminate spinel (TA and T, Millersville, Maryland; 356 × 356 × 12.7 mm^3) containing LiF as a sintering aid were fabricated using a 2-step manufacturing process. The first step densifies the starting powder via hot pressing (HP) and is followed by a second step of hot isostatic pressing (HIP) to achieve full density. The average grain size of this material is approximately 500 µm. The microstructure of this spinel can be seen via Scanning Electron Microscopy (SEM) in Fig. 1. Two different surface conditions were provided on the plates obtained from the manufacturer: an unpolished HP/HIP'ed finish, which was labeled "as received", and a standard commercial polish having an 80/50 (scratch/dig) finish. The latter finish is sufficient for the optical-transparency requirements in many window applications. A third surface finish was generated when the flexural test specimens were machined according to the guidelines in the American Society for Testing and Materials (ASTM)* standard C1161.[9]

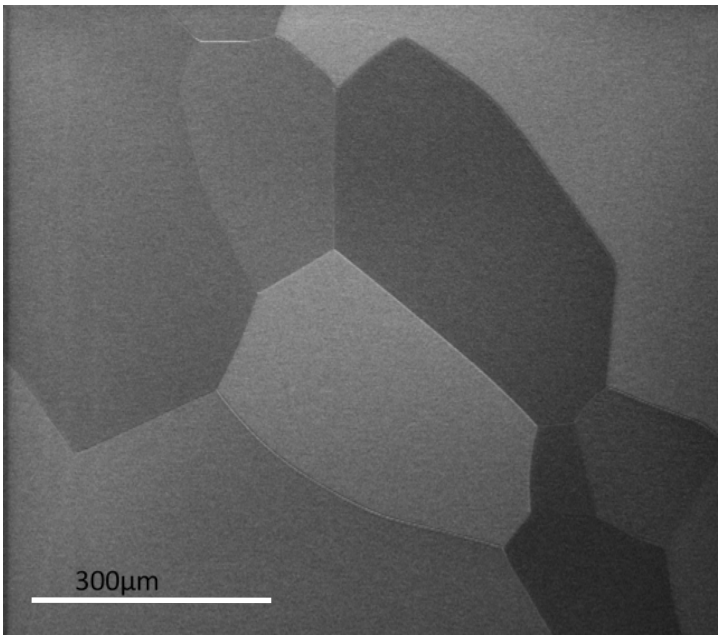

Fig. 1 SEM micrograph showing a representative section of the microstructure of the as-received hot-pressed/HIP'ed spinel plates

The flexure beam specimens machined from these plates were nominally 12.7 × 16.8 × 178 mm^3 in size. This size was chosen to preserve the 3:4 height-to-width ratio outlined in ASTM C1161 and to provide specimens with sufficient surface

* A Blanchard grinding step is used in the manufacturer's polishing procedure for achieving the finish required for an optically transparent material. However, Blanchard grinding is not permitted by American Society for Testing and Materials standard C1161 for the flexure specimens.

area to apply the glass coating. The as-received and polished surface finishes provided by the spinel manufacturer were maintained on one 16.8-mm-wide face of the respective flexure specimen during machining. This large flexure specimen was also shown to be the only beam specimen appropriate for determining the strength of this spinel.[1] The edges of all specimens were chamfered as per ASTM C1161.

A commercially available sodium aluminosilicate glass (PEMCO P-626-P; glass transition temperature, T_g, = 600 °C, fusion temperature, T_f, = 915 °C) was chosen as the glaze based on agreement between the coefficient of thermal expansion (CTE) of the glass, which was 7.2×10^{-6}/°C, and the CTE of the spinel, 7.3×10^{-6}/°C. This glass was supplied in the form of –325 mesh (<44 µm) powder. A slurry of glass was prepared with isopropyl alcohol at a solids loading of 50 weight percent. Prior to glass application, the specimen bars were completely cleaned with ethanol and then force dried with nitrogen gas.

One 16.8-mm side of each bar, with the appropriate surface finish, was coated with the glass slurry. This surface would then be the tensile surface in the 4-point loading configuration. The glass slurry was applied via a spray applicator (SATA Minijet 3000B spray gun) whose spray settings were 40-psi static and 25-psi dynamic. The glass slurry was applied to a wet-film thickness of approximately 250 µm, which would yield a fired-coating thickness of approximately 150 µm. The sprayed bars were air dried for 5 min and then placed into a glass-firing furnace to melt and anneal the glass coating following the firing and annealing cycle shown in Table 1. In addition, 4 of the polished large bars without a glass coating were heat treated in the same fire cycle with the glazed bars to examine the possible effects of the firing and annealing cycle on the flexure strength.

Table 1 The fire and anneal cycle to glass-coat spinel bars in air

Cycle	Rate (°C/min)	Ramp time (h)	Temperature (°C)	Hold (h)
1	5	3.0	905	3
2	2	0.3	865	1
3	3	0.2	830	1
4	2	0.38	785	1
5	2	0.5	725	1
6	2	0.63	650	1
7	1	1.67	550	1
8	1	1.67	450	2
End: Furnace cool to room temperature				

All baseline flexure tests, as well as those on the glazed specimens, were conducted at room temperature and humidity (<50%) in 4-point flexure following the procedures in ASTM C1161. The inner and outer spans were 66 and 132 mm, respectively, with a cross-head displacement rate of 1.8 mm/min.

Photographs were taken of the surfaces of uncoated samples and glazed specimens. Ultraviolet/visible-light (UV/VIS) spectra (PerkinElmer, Lambda 950 spectrophotometer) for each sample was generated from 200 to 3000 nm. Samples for UV/VIS transmission and photographic characterization were finely polished (1/4-µm final polish) on one side so the results were indicative of the surface finish of one side only. SEM (Hitachi 4700) and Energy Dispersive X-ray Spectroscopy (EDS) (EDAX Inc.) were used to examine the spinel–glass interface and determine any possible compositional interactions at this interface.

3. Results and Discussion

After the firing and annealing cycle, the resulting glass coating on the spinel had a smooth finish with no visible cracking due to the well-matched coefficients of thermal expansion. A small number of bubbles was observed in the glass coating on some of the specimens. These bubbles could potentially be eliminated by chemically lowering the viscosity of the glass or holding the specimens at the maximum temperature (905 °C) for a longer period of time. Increasing the firing and annealing temperature is not advised, because spinel has a tendency to opacify at higher temperatures as a result of pores within the grain boundaries bloating.[10]

The 4-point flexure-strength results are summarized in Table 2. The specimens with the HP/HIP and ASTM C1161 surface finishes have essentially the same flexure strength as the specimens polished by the manufacturer. Previous examinations of this coarse-grained spinel determined that grain boundaries in this material are extremely weak and serve as the strength-limiting feature.[1,11] As a result, it is not surprising the different surface-finishing procedures did not lead to any change in the flexure strength of this material. To further support this idea, additional flexure-strength tests were conducted on smaller test specimens, the 3 specimens outlined in ASTM C1161, with the surface finish prescribed in this standard. The flexure strength of these specimens was virtually identical to the flexure strength of specimens with the manufacturer's polished surface placed in tension.

Table 2 Summary of results of flexural-strength testing of coated and uncoated spinel bars; all specimens are the same "oversize" bars described in Section 2

	Uncoated			Glass coated		
Surface finish	**Strength (MPa)**	**Std dev[a] (MPa)**	**No. of samples tested**	**Strength (MPa)**	**Std dev (MPa)**	**No. of samples tested**
As-received HP/HIP'ed	85	14	5	75	7	4
ASTM	77	14	10	100	8	5
Polished[b]	71	8	9	128	33	9
Polished and heat treated	77	14	4		NA	

[a] Std dev: standard deviation
[b] Strength values for the polished and uncoated spinel are from Reference 1.

During strength testing the coating remained intact on the spinel surface throughout the entire loading process, even upon specimen fracture, indicating a strong bond between the spinel and the coating. Additionally, no contact damage was generated in the coating at any of the flexural loading points where the contact stress would be the maximum.

A direct comparison of the strengths of coated and uncoated specimens is more informative. As the surface finish of the spinel (prior to application of the glass coating) improves, the strengthening effect due to the glass coating increases. The strength of polished specimens with the glass coating increased by approximately 80% when compared with the polished specimens without a glass coating (128 MPa compared to 71 MPa).

Figure 2 shows an optical comparison of coated and uncoated samples. The optical-transmission quality of the ASTM-finish and HP/HIP'ed specimens is vastly improved by the addition of the glass coating. UV/VIS transmission curves for the coated and uncoated spinel specimens are shown in Fig. 3. As expected, the highest transmission was observed for the uncoated, polished specimen. This material is already considered to be of sufficient optical quality for a variety of window applications. After coating the polished specimen with glass, the transmission is reduced from approximately 75% to approximately 60% in the visible range. This is likely due to the following factors: 1) the presence of bubbles in the glass coating (the coating was not fully fined-out), 2) the interface-reaction product(s) that formed, and 3) the mismatch in refractive index between the spinel (n = 1.71), the glass (n = 1.25), and the glass–spinel-interface reaction products. Therefore, efforts are being made to eliminate the bubbles, minimize any interface reaction, and move toward a glass system with a higher index of refraction to more closely match the

refractive index of the spinel (i.e., lower the delta of refractive index). The transmission spectra measured on the specimens with HP/HIP'ed or ASTM finish were improved by the application of a glass coating (approximately 11% to approximately 40% for HP/HIP'ed, approximately 7% to approximately 38% for ASTM finish). This can be observed in an alternative manner by visual comparison of coated and uncoated samples (in Fig. 2), where the optical quality of the ASTM-finish and HP/HIP'ed specimens is vastly improved by the glass coating. This indicates that by addressing the concerns mentioned above, a glass coating may potentially decrease the number of polishing steps required to attain sufficient optical quality and strength of spinel windows for transparent-armor applications.

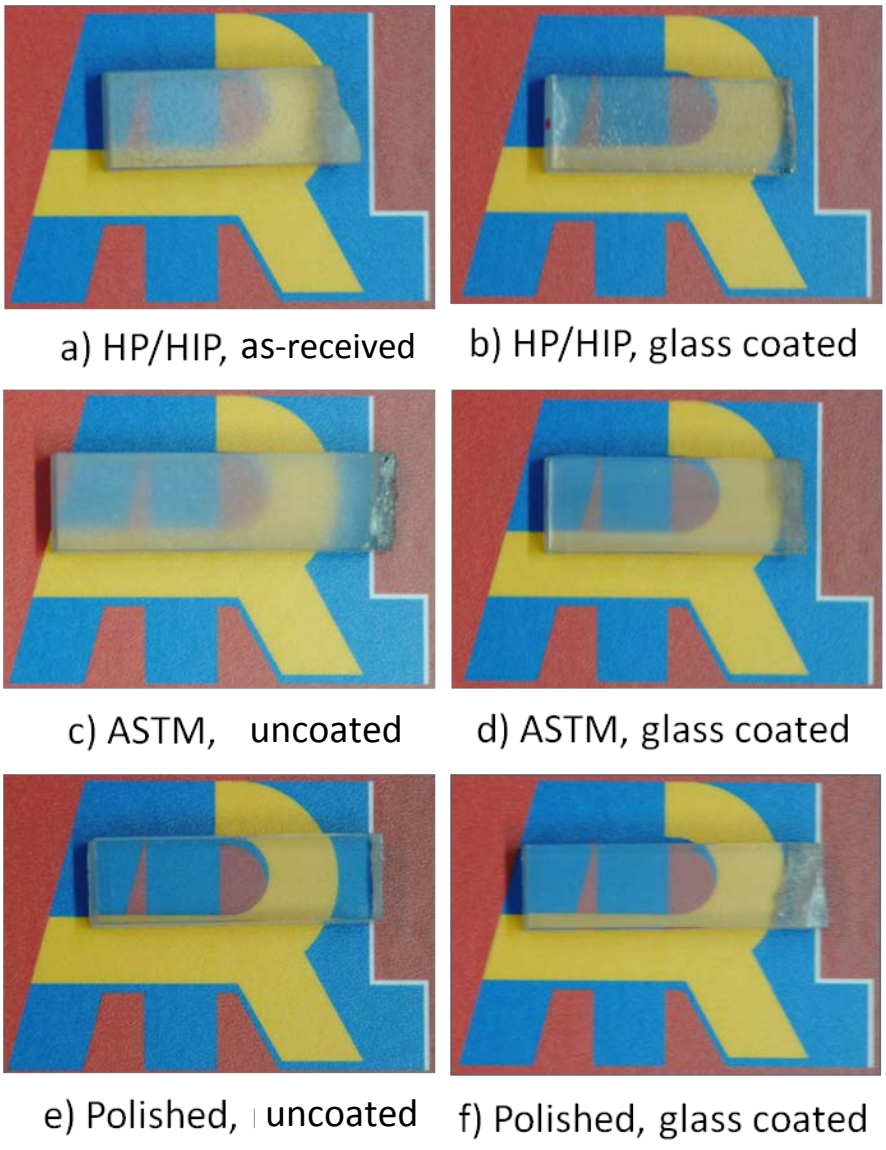

Fig. 2 Photographs qualitatively showing optical quality of uncoated- and coated-spinel specimens, all of which are in direct contact with the US Army Research Laboratory logo; bars' width is 16.8 mm

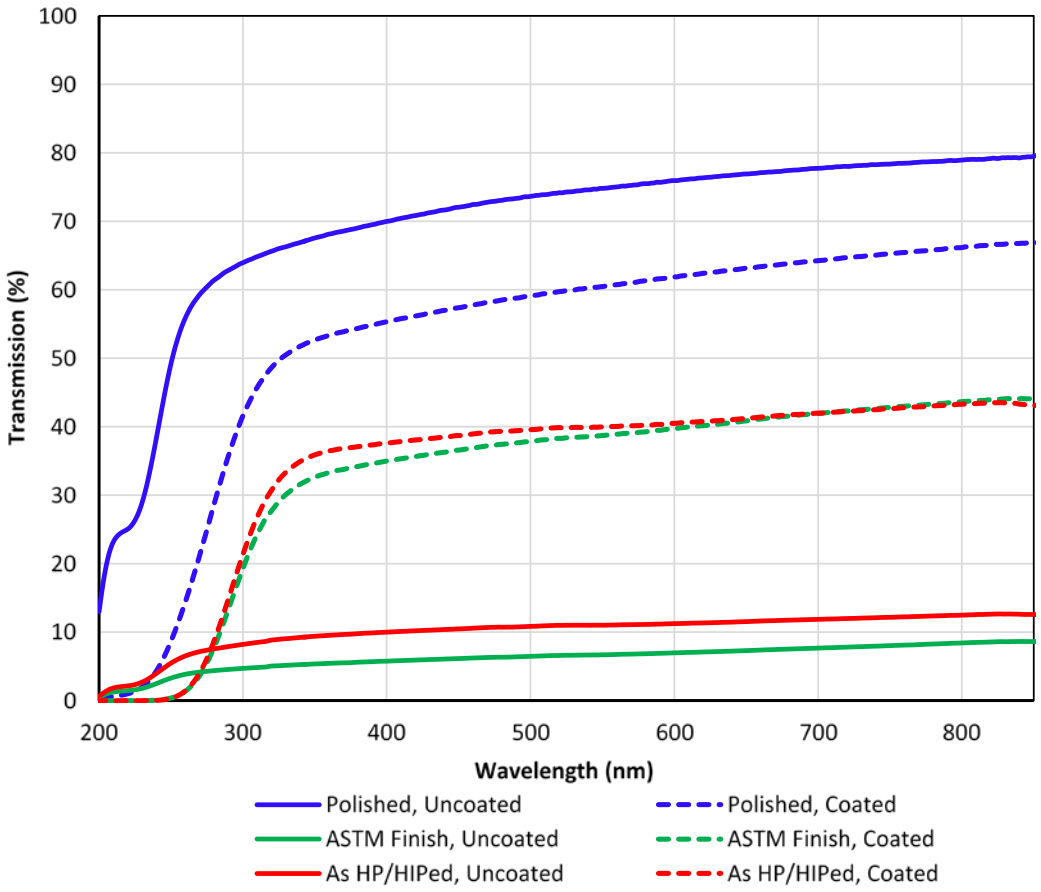

Fig. 3 UV/VIS transmission curves for all of the tested spinel specimens for 200–850 nm wavelengths

Figure 4 shows SEM micrographs of the spinel–glass interface of coated samples with all 3 different surface finishes. (Different magnifications are used on the images in Fig. 4 to better illustrate the concept.) In each case there are at least 2 distinct interface-reaction products. The lighter reaction product adjacent to the spinel appears to be faceted, especially in Fig. 4b, indicating there is a degree of crystallinity in this phase. The faceting may be due to preferential polishing of each phase present. The darker reaction product is adjacent to the glass. Gaps at the coating interface are also evident. These gaps could be due to incomplete wetting of the glass, the creation of gas via chemical reaction(s) occurring at the interface through volatilization, or, possibly, pull-out of material during the polishing operation. Despite these gaps, the glass coating is strongly adhered to the spinel, as there was no evidence of spalling or visible damage of the coating at the load pins as a result of the flexure-strength testing.

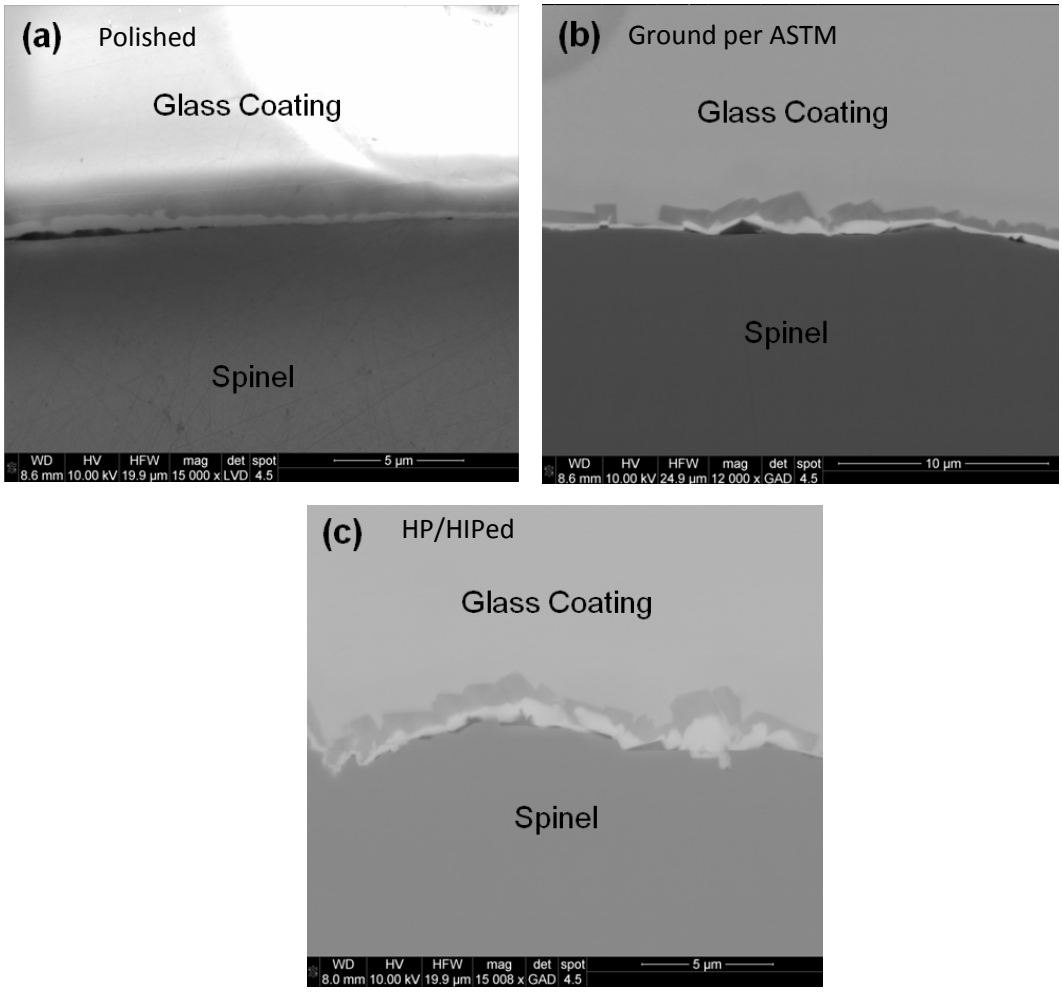

Fig. 4 SEM micrographs of the glass–spinel interface after heat treatment (Table 1); resulting interfaces of each surface-finish type—a) polished, b) ground as per ASTM, and c) HP/HIP'ed—all show existence of interface phases

To better understand the interface-reaction products, EDS line scans were performed across the glass–spinel interface of all 3 samples shown in Fig. 4. An example of the elemental composition determined by EDS is shown in Fig. 5. Although the exact nature of the interface-reaction products cannot be ascertained at this point, a few observations can be noted. The chemical compositions of the glass and spinel appear to be unchanged, indicating there is no detectable elemental diffusion into the applied glass or spinel. Any interdiffusion appears to be entirely within the interface-reaction zone. For example, while there is extensive aluminum diffusion out of the spinel, there appears to be much less magnesium diffusion out of the ceramic and into the interface region.

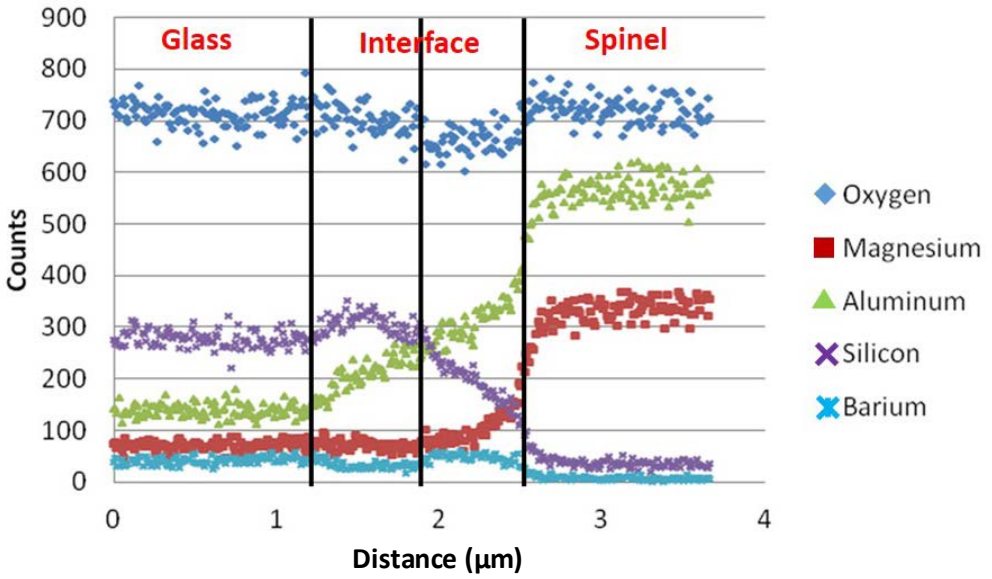

Fig. 5 Representative EDS scans across the glass–spinel interface showing relative change in chemical composition across the interface-reaction zone

4. Conclusions

The addition of a CTE-matched glass coating on polished spinel specimens leads to a flexural-strength increase of approximately 80%. This degree of strengthening was not realized in specimens with a HP/HIP'ed or ASTM C1161 surface finish. The strength increase was determined to be a result of the glass coating and not the heat treatment alone since the polished and heat-treated specimens had the same strength as the polished but uncoated specimens. Similarly, the optical quality of the polished spinel is not diminished appreciably by the addition of the glass coating, whereas the optical-transmission quality of the rough-surface spinel specimens is greatly improved. There is a reaction zone that forms at the glass–spinel interface. The existence and extent of this interface can be correlated to the processing conditions needed to form the glass coating (i.e., longer hold times and/or higher glass-processing temperatures will influence the degree of spinel dissolution into the glass). Further investigation is necessary to determine the nature of the reactions that are occurring at this location. The authors theorize that by employing an index-matched glass, coupled with a CTE match, the optical properties of the glass-coated spinel can be improved while simultaneously increasing the strength of the material. The use of such a glass coating could lead to a significant reduction in the amount of polishing necessary to achieve optical transparency and, hence, the overall cost of this spinel.

5. References

1. Swab JJ, Pavlacka R, Gilde G, Kilczweski S, Wright J, Harris D. Determining the strength of coarse-grained AlON and spinel. J Am Ceram Soc. 2014;97(2):592–600. DOI: 10.1111/jace.12698.

2. Fletcher PC, Tillman JJ. Effect of silicone quenching and acid polishing on the strength of glass. J Am Ceram Soc. 1964;47(8):379–382.

3. Rice RW, Mecholsky JJ, Becher PF. The effect of grinding direction on the flaw character and strength of single crystal and polycrystalline ceramics. J Mat Sci. 1981;16:853–862.

4. Schmid F, Khattak CP, Ivanoa SG, Felt DM, Harris DC. Influence of polishing on the biaxial flexure strength of sapphire at 600 °C. Proceedings of the 8th Department of Defense Electromagnetic Windows Symposium. 2000:356–363.

5. Varshneya AK. Fundamentals of inorganic glasses. 2nd ed. The Society of Glass Technology; 2006. p. 517–518.

6. Gentilman RL, McGuire PT, Fiore D, Ostreicher K, Askinazi J. Low-cost sapphire windows. In: Tustison RW, editor. SPIE Proceedings Vol. 5078: Window and Dome Technologies VIII; 2003. DOI: 10.1117/12.488241.

7. Harris DC. Materials for infrared windows and domes: properties and performance. Bellingham (WA): SPIE Optical Engineering Press; 1999. p. 195–212.

8. Kilczewski S, Pavlacka R, Wright JC, Swab JJ. Strength testing of glass coated magnesium-aluminate spinel. Paper presented at: 36th Annual Conference on Composites and Advanced Ceramics; 2012 Jan; Daytona Beach, FL.

9. ASTM C1161. Standard test method for flexural strength of advanced ceramics at ambient temperature. West Conshohocken (PA): ASTM International.

10. Reimanis I, Kleebe HJ, Rozenburg K. A review on the sintering and microstructure development of transparent spinel ($MgAl_2O_4$). J Am Ceram Soc. 2009;92(7):1472–1480.

11. Salem JA. Transparent armor ceramics as spacecraft windows. J Am Ceram Soc. 2014;96(1):281–289. DOI: 10.1111/jace.12089.

List of Symbols, Abbreviations, and Acronyms

ASTM	American Society for Testing and Materials
CTE	coefficient of thermal expansion
EDS	Energy Dispersive X-ray Spectroscopy
HIP	hot isostatic pressing
HP	hot pressing
$MgAlO_4$	magnesium–aluminate spinel
SEM	Scanning Electron Microscopy
Std dev	standard deviation
UV/VIS	ultraviolet/visible light

1 (PDF) DEFENSE TECHNICAL INFORMATION CTR DTIC OCA

2 (PDF) DIRECTOR US ARMY RESEARCH LAB RDRL CIO L IMAL HRA MAIL & RECORDS MGMT

1 (PDF) GOVT PRINTG OFC A MALHOTRA

2 (PDF) DIR USARL RDRL WMM E S KILCZEWSKI J SWAB